PICKLING, RINSING AND FLUXING OF STEELS BEFORE GALVANIZING

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In order to provide an adherent, defect free and long lasting galvanized coating on the steel surface, the pretreatment of surface is an important aspect in sequence of steps involved in galvanizing. Smooth and virgin surface having no trace of oxides acquires better coating. In all the galvanizing lines, whether batch or continuous, the pickling and rinsing of the surface is invariably carried out to remove oxides / mill scales and any trace of iron salts present there.

Pickling is carried out normally in hydrochloric acid or sulphuric acid or some times in mixed acid solutions. Certain advantages and disadvantages are associated with the pickling processes in both the acids. Hydrochloric acid for instance, is considered superior to sulphuric acid in respect of providing smoother and brighter pickled surface, less hydrogen blistering, better cold working, less iron carryover in galvanizing bath and effective at lower temperatures of operation but at the same time is highly objectionable from pollution, corrosion, transportation and storage point of view. Sulphuric acid on the other hand is less corrosive and harmful to human beings and to the surrounding structures. It is transported in a more concentrated form (98% compared to 35 % of hydrochloric acid), but suffer from the drawbacks of higher temperature bath, production of an uneven, blistered and smutty surface, thus making the galvanizing and other surface coating processes uneconomical. It has been established by many investigators that hydrochloric acid pickling of steels is always superior to sulphuric acid pickling, its volatility which is enhanced by the rise in temperature, acid strength and iron content in the bath, is however, of main concern and creates problems in the pickling process. Due to these problems associated with the hydrochloric acid, sulphuric acid is still in use in many steel plants inspite of the inherent drawbacks described above.

During the recent years, attempts have been made to use mixed acid pickling operation. Another approach is to add sufficient chloride ions in the form of salts in sulphuric acid solutions. This avoids the drawbacks associated with the hydrochloric acid and provides beneficial effects associated with the hydrochloric acid, such as:

* chloride ions being more surface active and more water soluble than sulphate ion, dislodges the latter from the surface and makes the surface free of loose iron salts. This avoids smut formation on the surface.

the gaseous hydrogen facilitates delamination of scale which has lost contact with the steel surface. During pickling process, the first and second stages i.e. the diffusion of acid through fissures to the base metal and reaction of base metal with acid producing hydrogen, determine the kinetics of the scale dissolution. To facilitate these steps, an additive present in the pickling bath, must posses the following properties:

a) They should reduce the surface tension of the liquid to a considerable extent so that acid can easily penetrate through the fissures and defects,

and b) The depolarizing action for cathodic reaction should be catalyzed by the additives so that the potential may attain a higher value to facilitate the hydrogen evolution reaction. These aspects have been discussed in detail under a separate sub- heading of lecture in economizing the pickling process by use of inhibitors.

Choice of Acid for Pickling:

As discussed earlier, hydrochloric or sulphuric acids are generally employed for pickling of steel articles in galvanizing plants. However, if overall aspects are considered, it is found that hydrochloric acid pickling has an edge over sulphuric acid pickling. However, in case, the plant is unable to switch over from sulphuric to hydrochloric acid pickling, as is the case with many galvanizers who use sulphuric acid, the efficiency of pickling operation can be enhanced by adding sodium chloride in sulphuric acid bath. Following positive aspects are observed as a result of addition of sodium chloride in sulphuric acid baths:

a) Pickling rate is faster;

b) Bath operates at lower temperature;

c) Metal-loss is reduced;

d) Acid consumption rate is reduced;

e) Air pollution is minimized;

f) Salt tolerance in the pickling bath is increased;

g) Iron carryover in the galvanizing bath is less and therefore, the dross formation is reduced;

h) Surface is brighter and smoother,

and i) Zinc consumption rate per unit area is reduced.

It is pertinent here to discuss in brief, on the causes of positive role played by the addition of sodium chloride in the sulphuric acid baths. Since the surface activity of chloride is higher than sulphate ions, it helps the acid quickly to reach the base metal. Accelerating effect of chloride on scale dissolution is also attributed to its ability to form complexes of the type $(FeOHCl)_{ads.}$ with hydrolysed iron atom:

Fe-O-Fe + HOH -----> 2 [FeOH]

$$Fe(OH) + Cl \quad \text{-----}> \quad [FeOHCl]_{ads}^{m-}$$

this complex dissolves faster in the acid solution than the corresponding complex formed in case of sulphuric acid which produces $[FeOHSO_4]_{ads}^{m-}$.

Once the scale is dissolved, chloride ion depletes the sulphate and hydroxyl ions from the base metal and retards the reaction by passivation effect.

PICKLING DEFECTS:

Following Defects are encountered during the pickling of steel in acid solutions:

a) Underpickling

This arises due to weak acid concentrations or higher content of iron salts in the bath. To achieve good quality of pickling, the iron salt under normal parameters of pickling should not go beyond 8-10% in the bath. The ideal strength of acid solution in the bath is 20% sulphuric acid or 15-20% hydrochloric acid. Black spot in galvanizing generally arises due to this defect.

b) Overpickling

This arises due to use of inferior quality of inhibitors in the bath. An overpickled surface causes excess zinc consumption and also accelerated attack of molten zinc with the steel surface. An increase in coating weight is observed. This defect can be avoided by using proper ambiodic type pickling inhibitors in the acid bath.

c) Hydrogen blistering:

As explained earlier, during the reaction of steel with acid solutions, hydrogen evolution reaction takes place. In ideal conditions, the liberated hydrogen should be evolved in gaseous form. However, a part of the hydrogen atom, instead of combining to from gaseous molecule, penetrates inside of steel and accumulate in lattices.

$$H^+ + e \quad \text{-----}> \quad 1/2\ H_2$$

$$1/2H_2 + Fe \quad \text{-----}> \quad Fe\text{-}H_{ads}$$

$$Fe\text{-}H_{ads} \quad \text{-----}> \quad Fe_{Hads}$$

Since the areas of lattices are extremely small, the pressure due to the diffused hydrogen inside the lattices becomes very high. The gas embrittles the metal and we get defects. This problem can be avoided by using a film forming type strong inhibitor in the acid solution. No trace of strong cathodic polarizers such as, As, Sb, Sn, sulphur compound etc. should be present in the acid bath. These elements accelerate the process of hydrogen absorption inside the lattices of steels.

d) Smutty Surface:

As mentioned earlier, for the pickling operations to proceed smoothly, some extent of dissolution of parent metal with acid solution is essential. During the process of dissolution of base metal, the cementite part of the structure of carbon steel becomes cathodic (less reactive) than ferrite part. These cementite part after pickling remain intact with the surface although we feel that the pickling is over. A smutty surface thus appears due to the presence of unreacted cementite on the surface. During galvanizing, the cementite is transferred to the galvanizing bath and forms dross.

To get rid of this problem, two approaches are adopted. In one approach, steels' potential is raised sufficiently noble so that cementite is dissolved in solution. In another approach, strong cathodic depolarizers are added in the bath to increase the fugacity of hydrogen on the surface resulting in reduction of cementite into hydrocarbon and iron.

USE OF INHIBITOR TO ECONOMIZING PICKLING

The pickling process can be economized to a considerable extent by using suitable inhibitor in the acid bath. the benefits that can be derived by use of a proper inhibitor are:

* Reduction in acid consumption,
* Reduction in metal loss,
* Increase in productivity,
* Creating a pollution free congenial working shop floor,
* Decrease of pollution load in discharge water,
* Decreasing the coating weight,
* Decreasing the rejection of galvanized material due to hydrogen blistering.

Corrosion inhibitors are organic based chemical compounds having active adsorption centres at the elements such as, S, N, O and at delocalized electrons etc. They are normally high molecular weight organic compounds, completely soluble in acid solutions. Different types of inhibitors are employed for different acids. For hydrochloric acid solutions, e.g. amino compounds are quite effective. In sulphuric acid, amine and sulphur compounds are effective. To achieve improved protection, synergistic mixtures of inhibitors are employed.

It has been established that the selection of a proper inhibitor for particular pickling can save crores of rupees in terms of saving of acid and metal loss. One kg of iron loss can be reduced by reducing 1.5 Kg of acid consumption (sulphuric acid). In case of HCl pickling a reduction in acid consumption of 4.5 Kg would reduce 1 Kg of iron loss. A good example is the impact of use of NML-Metasave,

a pickling inhibitor based on high molecular weight organic polymeric compounds, on economy of pickling. Economical benefits derived by the use of NML - Metasave in different steel plants are summarized in Table I to III and in figure 2. It is seen from these Tables that the money saved by the plants due to the use of a properly designed inhibitor is substantial in comparison to the other inhibitors.

The above benefits derived by the plants are achieved due to the balanced structure of NML-Metasave. This provides optimum protection to the steel surface in lower as well as higher acid strengths and also applicable to almost equal extent in protection when used lower and higher temperatures of the pickling bath. The productivity is found to be increased due to its effect in lowering the surface tension of the solution and thus facilitating the easier penetration of acid solution through the fissures and defects of mill scales/oxides. A stable film form on the bath surface helps in reducing air pollution. Hydrogen entry into the steel is negligible owing to the absence of any strong cathodic polarizers (poisons for re-combination of step of hydrogen atoms) in the composition of metasave.

EFFECT OF ACCUMULATION OF IRON IN THE BATH

With the increase of iron content of the bath, the pickling efficiency i.e. the pickling rate decreases. This is owing to the blocking effects of iron salts in fissures of the mill scales and thus hindering of the transport of the acid beneath the scale and hence the negligible reaction with the base metal surface. No hydrogen is liberated and therefore, the reductive dissolution of the scale is hindered. Another cause of reduced pickling rate is due to the accumulation of Fe^{3+} in the bath with scale dissolution which results in onset of parallel cathodic reaction:

$$Fe^{3+} + e^- \text{ ------> } Fe^{2+} \qquad (1)$$

alongwith the usual hydrogen evolution reaction i.e.

$$2H^+ + 2e^- \text{ -------> } H_2 \qquad (2)$$

Due to the onset of reaction 1, the corresponding anodic reaction ie, the steel dissolution becomes quite fast. Negligible hydrogen evolution reaction i.e. 2, takes place and therefore, the reductive dissolution of oxide/scale does not take place. The above two factors i.e. the transport of acid to the base surface and onset of parallel cathodic reaction (1) conjointly influence the rate of pickling and we get reduced rate of pickling, increased metal loss and some times underpickling also. Yet, another reaction for stifling effect on pickling due to increase in iron concentration in the bath is due to the reduction in extent of ionization of acid and hence reduced concentration of availability of H^+. Ionization of acid can be written as:

$$HA \quad === \quad H^+ + A^-$$

$$K = \frac{[H^+]\,[A^-]}{[HA]}$$

As the iron salt in the bath (FeA, where A, is anion in acid i.e. SO_4^{2-}, Cl^-, PO_4^{3-} etc.) and hence A^- increases, the ionization of HA decreases to maintain the equilibrium. This results in less availability of H^+ which plays a main role in the pickling operation. To minimize the following remedial measures can be adopted:

a) Continuous depletion of iron salt by low temperature crystallisation or electrolytic deposition

b) Addition of suitable surfactant in the bath to effect a drastic reduction in surface tension of the solution

c) Addition of strong complexing agent in the bath so that Fe^{3+} is complexed and does not take part in the parallel cathodic reaction.

For bigger plants, technique (a) is quite useful and many steel plants such as Rourkela, Bokaro, etc. adopt it. Smaller picklors can implement technique (b) and (c) and proper selection of surfactant and complexonents can be suggested by systematic study of the temperature of operation, type of pickled products and iron concentration in the bath etc.

RINSING

During pickling of steels, loose iron salts remain adhered to the surface. If these salts are not removed from the surface before dipping in the galvanizing bath, they get transferred to the bath and combine with molten Zn to form dross. In dross (which is a compound of zinc and iron) one part of iron can combine with 24 parts of zinc. Thus removing these salts before taking the articles into the galvanizing bath is an essential steps to reduce the dross formation.

It has been estimated that out of total dross formation during galvanizing, about 90 - 95% of iron comes from the galvanizing articles and the rest comes from the galvanizing pot. Out of this 95% about 50-55% is transferred as a result of loose salt present on the surface after pickling. In a batch type of operation of sheet galvanizing, we have observed that a direct relationship exists between the galvanized surface area and amount of iron transferred in the galvanizing bath (Figure 3).

The problem of iron carryover from pickling stage can be reduced by efficient rinsing operations. Hot rinsing is always superior to room temperature rinsing of pickled product. We have observed that the use of certain sequestering agents in rinsing bath efficiently reduce the carryover of iron salt in

galvanizing bath: One molecule of these sequestering agents combine with 20- 30 molecules of iron and the complex so formed is highly soluble in water even in room temperature. Some lab scale test results are summarized in tables IV & V and figures 4 & 5.

FLUXING

Adherence and type of coating of zinc on steel surface is largely decided by the type of surface that reacts with molten zinc. An oxide free steel surface acquires an adherent and defect free galvanized coating. The removal of oxide from the steel surface is performed in the following two ways:

I) Bathless process:

After pickling and rinsing, the material is dried and passed through a reducing atmosphere (hydrogen atmosphere) at elevated temperature. This reduces the oxide present on the steel surface and it acquires an adherent and good quality coating when dipped in molten zinc bath. Many modern galvanizing plants are operating based on this process. The benefits associated with this technique are:

a) Reduced air pollution in comparison to the process based on the use of fluxes,

b) No handling of corrosive liquids,

c) Reduced dross formation as no corrosive agent is added in the molten zinc bath.

II) Fluxing process:

After pickling and rinsing, the surface of steel article is extremely active and therefore, quickly oxidizes to form thin layer of oxide. This oxide not only hinders the coating formation but also costs galvanizers dearly by increasing the dross generation. To make the steel surface active and free of oxides they are fluxed using active chloride salts. This can be achieved in two ways:

a) Prefluxing:

Used in dry galvanizing process. In this technique, the article to be galvanized is treated in water solution of zinc chloride-ammonium chloride mixture at about 70- 80°C for about a minute and then dried in drying oven at 100 - 120°C prior to dipping in galvanizing bath.

b) In-situ fluxing:

Used in wet galvanizing process. In this technique a solid mixture of zinc chloride-ammonium chloride is added on the top of the molten zinc bath. The article to be galvanized directly passes to the galvanizing bath after pickling, rinsing and drying.

Action of fluxes

Normally, zinc chloride-ammonium chloride based fluxes are employed in wet as well as dry galvanizing. Other fluxes based on triple salts have been developed and they are found to be superior

than the binary mixtures of conventional fluxes. In the wet galvanizing process, a flux blanket on the surface of the molten zinc bath is used to remove the impurities such as oxides, chlorides, sulphates and sulphides, from the steel and molten zinc bath surface. In fluxing operations, the release of hydrochloric acid and zinc hydroxy acid are extremely important reactions. These acids are produced due to the decomposition of NH_4Cl and combination with $ZnCl_2$.

$$NH_4Cl \quad \text{----->} \quad NH_3 + HCl$$

$$ZnCl_2.2H_2O + HCl \quad \text{------->} \quad \{HCl(OH)_2\}H_2.ZnCl_2$$

Hydroxy acid

Zinc hydroxy acid is extremely acidic and quickly reacts with oxides present on the molten zinc layer and steel surface to form corresponding chlorides.

It is important to mention here that the use of simple NH_4Cl as flux in galvanizing does not function properly. It is due to the reason that the solid NH_4Cl sublimes below 100°C and does not decompose into hydrochloric acid and ammonia. In order that NH_4Cl decomposes into the two components, it should be dissolved in a solvent whose boiling temperature is above 100°C. $ZnCl_2$ having water of crystallization is the appropriate solvent for decomposition of NH_4Cl and to form hydroxy acids. These acids are stable at the top of the molten zinc (temperature 350°C) and act extremely well as flux. The action of mixed flux ($ZnCl_2$ + NH_4Cl) in prefluxing process can be explained as follows:

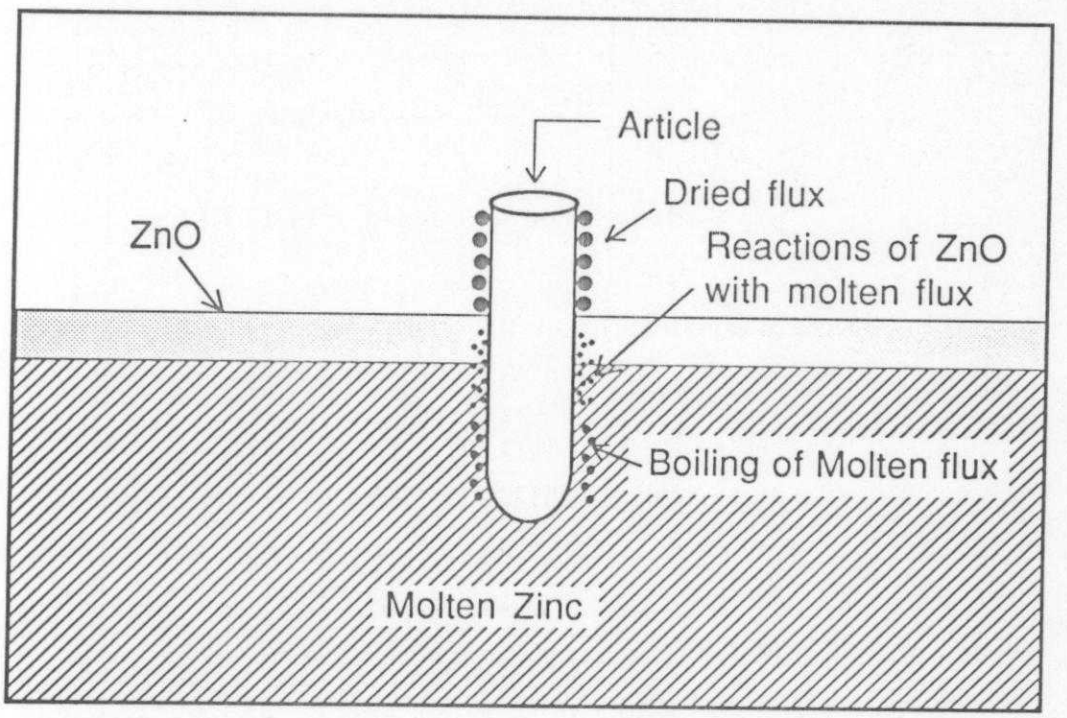

Fig.
Action of Tripple Salt based fluxes during Dry Process of Galvanising

Fig. 6. Action of flux during dry process of galvanizing

The article to be galvanized is first treated with an appropriate concentration of flux. It is than dried at about 110-120°C. During the process of dipping of the articles in molten zinc bath, the flux first melts at the top of bath (temperature 350°C). With rise in temperature (the articles going dipper into the bath) the preflux starts boiling and hydroxy acids are form. These acids react with ZnO on the molten zinc surface and iron on the steel surface to provide cleaner surface for galvanizing.

Drying of prefluxed articles

The prefluxed articles should be dried at 110 -120°C but below 150°C. This is due to the reason that the water of crystallization of $ZnCl_2$, which is an important ingredient in the formation of hydroxy acid, evaporates above 150°C. If drying is performed below 100°C, the moisture trapped in the flux is transferred in the galvanizing bath and explodes due to the formation of steam. This blows away the film of flux formed on the steel surface and may cause black spots.

Ratio of NH_4Cl-$ZnCl_2$ in fluxes

It is evident from the above discussion that the performance of fluxes in activating the steel surface and removing the impurities from the top of molten zinc is largely governed by the boiling temperature of the fluxes. the boiling temperature of the binary mixture of zinc and ammonium chloride is dependent on the weight ratio of the constituents present in the mixture. A phase diagram showing the effect of weight ratio of constituents in mixture of ammonium and zinc chloride on the boiling temperature is shown in figure 7. It is evident from this figure that the boiling point of the mixture decreases with increase in proportion of NH4Cl. After a 10 : 90 ratio of NH_4Cl : $ZnCl_2$, it attains a constant temperature of about 350°C. This was the reason that during early seventies, above ratio was maintained in fluxes. However, in latter stages, this type of fluxes were taken off from the market due to the following reasons:

a) Due to the presence of less amount of NH_4Cl in fluxes, sufficient amount of HCl was not produced. This restricted to the formation of hydroxy acids which are important ingredient in fluxing.

b) The ratio was quickly disturbed due to decomposition of NH_4Cl and thus resulting in an increased temperature of boiling (above the kettle temperature). To overcome this problem, higher ratio of NH_4Cl were recommended for fluxing. The concept of ammonium chloride number (A.C.N.) for fluxes was introduced. A.C.N. is defined as:

$$\text{A.C.N.} = \frac{\text{Weight \% of ammonium chloride}}{\text{Weight \% of zinc chloride}}$$

In early eighties. it was suggested that an A.C.N. value of 1.75 to 2.5 was the most appropriate for

effective fluxing. This was based on the logic that:

a) The boiling point of flux having ACN of 1.75-2.5 is maintained at about 350°C

and b) Sufficient hydroxy acids are formed and resulting in an efficient fluxing.

The above flux composition, indeed, provided excellent result so far as quality of galvanizing product was concerned. No black spot appeared during the galvanizing. But two vital aspects were not considered. The first and the most important aspect was severe corrosive attack of NH_4Cl on the steel and zinc in its aqueous as well as in molten phases. NH_4Cl is extremely corrosive to steel and thus causes a high rate of dross generation and thicker coating during galvanizing (Figure 8). The second aspect which goes against the use of this type composition is excessive evolution of white fumes of NH_4Cl which is dangerous and highly objectionable from pollution point of view. Many galvanizers, however, still use this type of mixture as flux during the wet as well as dry galvanizing processes.

DEVELOPMENT OF TRIPLE SALT BASED FLUXES

The above discussions clearly indicate that the fluxes based on neither low ACN nor high value of ACN are ideal for fluxing. Moreover, a flux having its components as individual independent identity in the mixture does not yield the desired results of fluxing. To overcome these problems, a new concept of synthesising a simple molecule having a fixed value of ACN fluxes has been developed during the recent years. An ideal flux in this series is a compound based on triple salt fluxes. The unique properties associated with such fluxes are:

i) It is a single molecule compound having a fixed ACN (1.17).

ii) The boiling temperature is constantly maintained in a range of about 350°C.

iii) They are least corrosive towards the galvanizing articles and also towards the molten zinc.

iv) White fumes evolution during galvanizing is negligible.

v) It is a single pack system and do not need any extra care as required for handling of $Zncl_2$.

vi) Surface tension of water solution of the triple salt based fluxes is extremely low and therefore, allows the penetration of the solution in intrinsic parts of the galvanizing articles in dry process.

vii) As decomposition temperature is quite high, no pungent smell of ammonia is felt during fluxing and drying. This gives a great relief to the crane operators.

The above positive factors associated with a triple salt based fluxing make the galvanizing quite economical and environmental friendly. Although developed countries had been using triple salt based fluxes since long back, the technology for manufacture of triple salt fluxes was not available in India.

Recently, National Metallurgical Laboratory, Jamshedpur, has developed the technology for the manufacture of this type of flux which has been patented and designated as NML-Galvaflux. It is under evaluation at the galvanizing line of Tata-Tubes, Jamshedpur. The product is commercially available now. Some observations of this evaluation are summarized in Table VI.

Some chemical reactions involved during fluxing and galvanizing:

$$Zn(NH_4)_3Cl_5.4H_2O \xrightarrow[\text{On bath surface}]{} Zn(NH_3)_2.Cl_2.2H_2O + \underbrace{\{HCl(OH)_2\}H_2}_{\text{Hydroxy acid}} + 2HCl + NH_3$$

$$\underset{\text{(Deep in the bath)}}{Zn(NH_3)_2Cl_2.2H_2O} \longrightarrow \{ZnCl_2(OH)_2\}H_2 + 2NH_3$$

$$\underset{\text{(On the bath surface)}}{ZnO + \{ZnCl_2(OH)_2\}H_2} \longrightarrow \underset{\text{(Zn-Oxychloride)}}{ZnO.ZnCl_2} + 2H_2O$$

Above oxychloride is in soluble in molten zinc and forms skimmings.

$$FeO + \{HCl(OH)_2\}H_2 \longrightarrow FeO.HCl + 2H_2O$$

above iron oxychloride is insoluble and forms skimmings

The above reactions clearly indicate that the formation of oxychlorides by the decomposition of fluxes is a pre-requisite for a meaningful use of a flux. A triple salt based fluxes meet all the requirements for the formation of the above mentioned oxychlorides. It is also observed from the above reactions that the dross formation is minimized due to the reactions of the oxychlorides with oxides of zinc and iron and thus forming skimming. It is therefore necessary that sufficient flux concentration should be present on the top of the molten zinc as well as on the surface of the articles to be galvanized so that enough oxychlorides are formed to take care of dross forming impurities and bring out them as skimming. Use of a higher concentration of triple salt based fluxes on the top of molten metal or in pre-fluxing bath is, therefore, always beneficial. However, a flux based on physical mixture of $NH_4Cl+ZnCl_2$ if used in excess amount either as pre-flux or as top flux is harmful and results in excessive dross generation, pollution and higher fluxing cost.

Maintenance of concentration of triple salt based fluxes

In wet galvanizing, the concentration should be maintained to such an extent that the surface is covered with a foamy layer and no black spot appear during the galvanizing. In dry galvanizing, our observations reveal that a concentration between 20-35% in the pre-fluxing bath is quite effective. The

concentration should be decided on the basis of gauze of materials and type of steel to be galvanized.

Accumulation of iron salt in the bath

It is general belief that an increase in the iron content of the fluxing bath, has an adverse effect on galvanizing process and results in an increased dross generation. while this consideration is indeed true for a conventional type of fluxes where a remote chance exists for the formation of oxyacids (due to instability of fluxes at galvanizing temperature) as stated above, in case of triple salt based fluxes, however, an increase in iron content of bath has no adverse effect. It rather helps in the fluxing action. Iron salts are converted as iron chloride and they sublime at the galvanizing temperature. These chlorides do not take part in dross formation and mostly either sublime or form iron oxychloride (FeO.HCl) and floats on the surface as skimming. De-ironing of fluxing solution is therefore, not only unnecessary but can only be carried out at a great loss of flux and wastage of reagents and manpower.

pH of the fluxing bath:

pH of the fluxing bath remains at 3.5-4.5 if its ACN is properly maintained (most appropriate ACN is 1.17). Extra addition of HCl in the bath is not recommended. Extra added HCl evaporates during fluxing and drying and adversely affects the surrounding structures and health of shop floor personals. We have observed that the presence of SO_4^- in the fluxing bath helps in quicker drying of fluxed articles.

Presence of surfactants and rare earth chlorides:

Modern fluxes based on triple salt contain non-ionic organic surfactants and rare earth metal chlorides. These substances help in reducing the surface tension of the flux solution (in dry galvanizing only) and also in increasing the life of the flux film formed on the surface.

Chloride free fluxes:

In molten zinc, aluminium addition upto 0.005 wt% are maintained in batch type of galvanizing processes to have a brighter coatings. A larger addition of aluminium in the bath has a pronounced effect on alloy layer growth and also corrosion resistance of coatings. In Galfan and Galvalum process, about 5 % of Al is maintained in the bath. The higher proportion of Al in the bath is a common practice in Sendzimer continuous strip galvanizing process where no flux is employed and strips are first annealed in controlled atmosphere and then deoxidized by putting them in reducing atmosphere. In batch process, however, the Al addition is limited upto 0.005 % and any increase in Al content above this, results in appearance of black spots in the galvanized products. This is due to the reaction of fluxes with Al_2O_3 on the surface.

$$Al_2O_3 + 6NH_4Cl \text{ -------> } 2AlCl_3 + 6NH_3 + 3H_2O \quad (3)$$

In the above reaction, all the three constituents of products formed by the action of NH_4Cl with Al_2O_3 are volatile and the bath, ultimately becomes free of flux and alumina. This result in poor fluxing operation and appearance of black spots due to blowing away of coating by gases formed as shown in reaction (3).

To overcome the above problems, there has recently been a surge of interest in development of chloride based fluxes. Some fluxes having organic fluorides and other organic surfactants are reported to function with the baths having Al upto 5 %. These Studies are still trade secrets of some U.S. companies and details are not available in the open literature. NML is trying to develop such fluxes for batch type of operations.

ACKNOWLEDGEMENTS

Some of the data presented in this lecture have been generated at the plant scale operations of Tata-Steel, Tata-Tubes, TCIL and Rourkela Steel Plants. The author is thankful to the managements of the above companies for providing necessary facilities to generate the data in their plants. The author expresses great sense of gratitude to the Director, NML, Jamshedpur for encouragements and some colleagues who provided tremendous help in generating the above data.

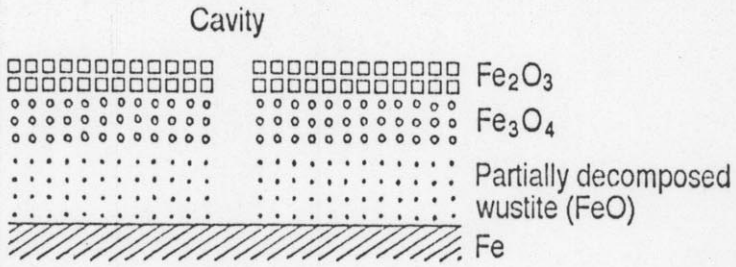

FIGURE 1. *Schematic of mill scale formed on hot-rolled steels.*

. An electrochemical cell is formed in which the steel (base metal) behaves as the anode and the magnetite and wustite behave as soluble cathodes (due to reductive dissolution).[11] Magnetite acts as a cathodic depolarizer, whereas hematite suffers from negligible dissolution and has little effect on the cathodic process. Magnetite is dissolved partially during the cathodic dissolution of wustite and magnetite by:

$$Fe \rightarrow Fe^{2+} + 2e^- \quad (1)$$

$$FeO + 2H^+ + 2e^- \rightarrow Fe + H_2O \quad (2)$$

$$Fe_3O_4 + 8H^+ + 8e^- \rightarrow 3Fe + 4H_2O \quad (3)$$

Since the wustite is removed by the acid, the contact between the magnetite and metal is lost, and the scale is delaminated due to hydrogen evolution at the base metal surface.

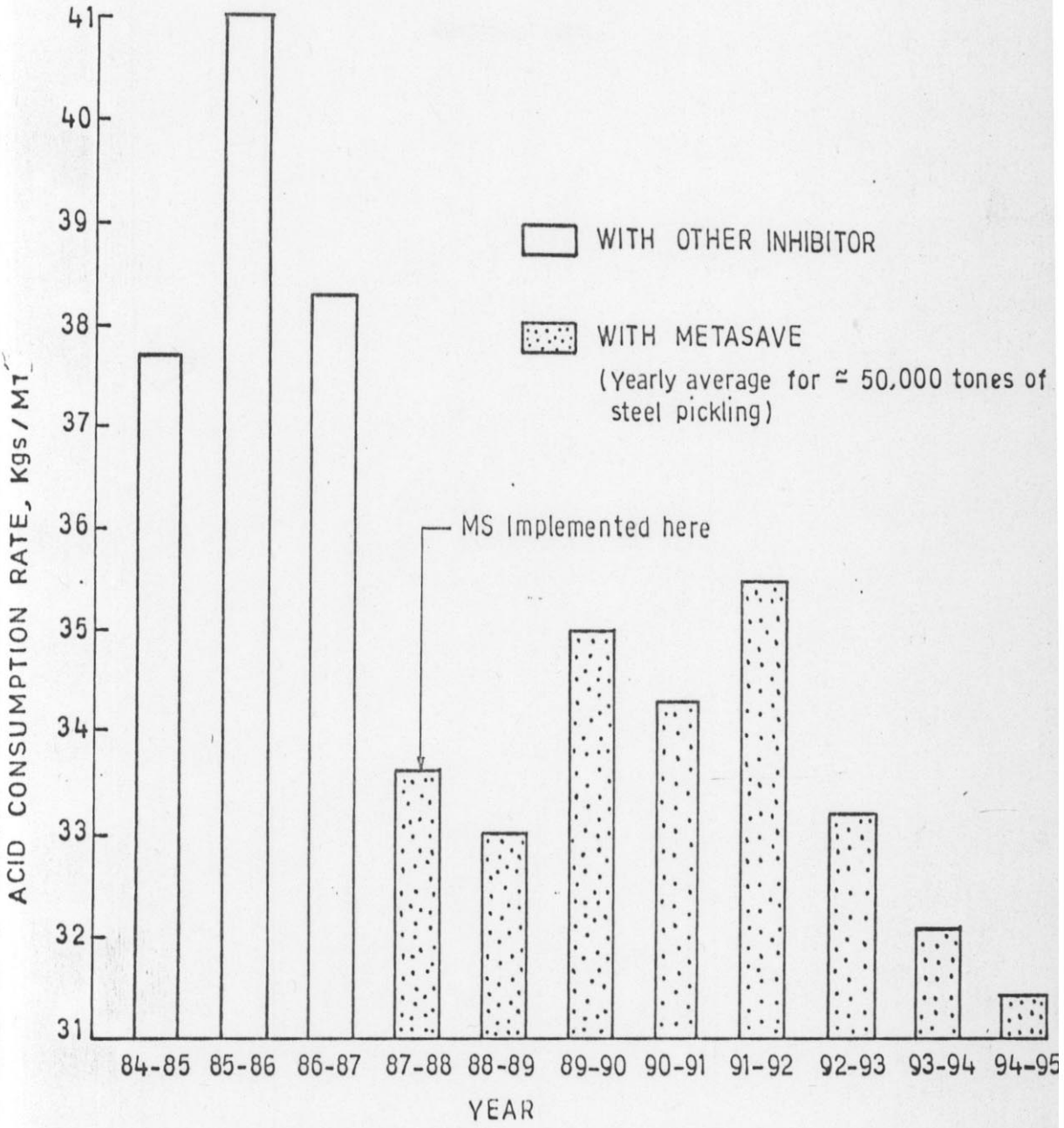

FIG.2: Year-wise acid consumption rate for Tata steels pickling line.

IRON PICKUP IN GALVANIZING BATHS

(a) BY ATTACK OF MOLTEN ZINC ON GALVANIZING POT (made of Steel)

(b) BY GALVANIZING SURFACES

IRON PICK-UP IN STEPS (b) IS MANY FOLD HIGHER THAN IN STEP (a)

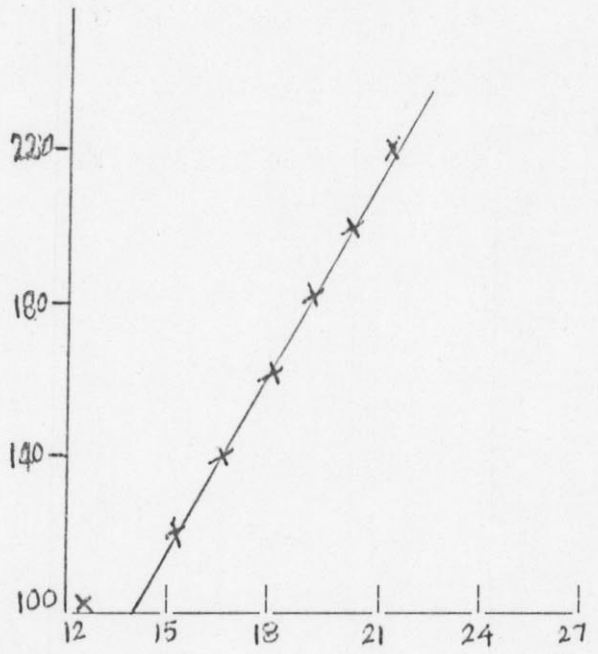

FIG.3. RELATION BETWEEN DROSS GENERATION AND QUANTITY OF PRODUCTION

* THE PLOT SHOWS THAT IRON PICK-UP IS DIRECTLY PROPORTIONAL TO THE SURFACE AREA EXPOSED TO MOLTEN-ZINC.

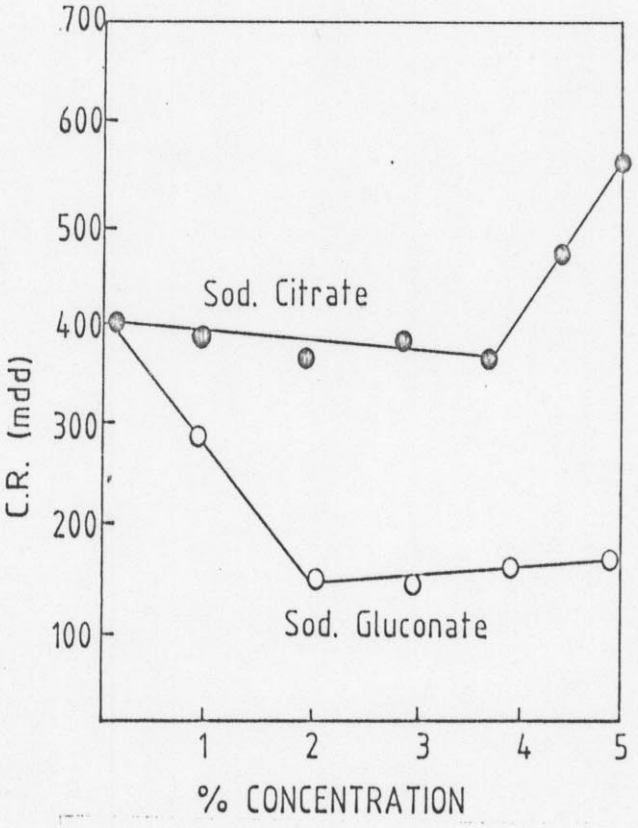

Figure-4: Corrosion rate vs. concentration of sodium gluconate and sodium citrate in 0.5% HCl and 5% $ZnCl_2$ solution.

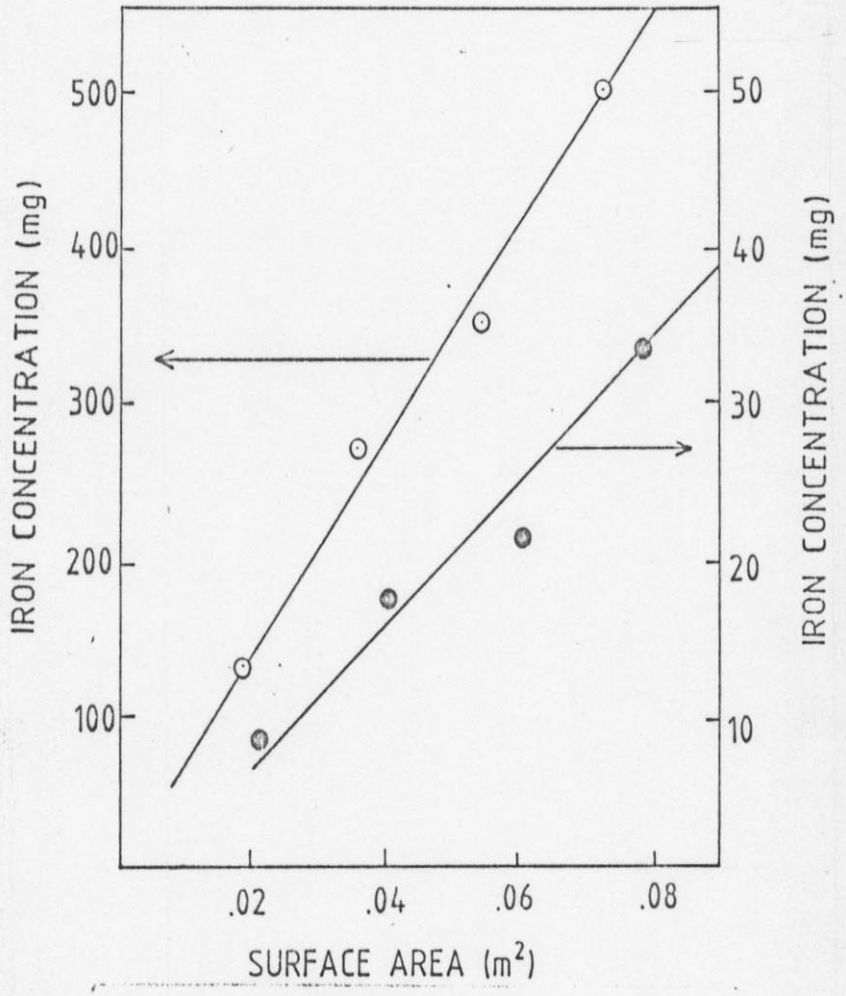

Figure- 5: Effect of surface area on iron carry over Rinsed in water, exposed to complexing solution.

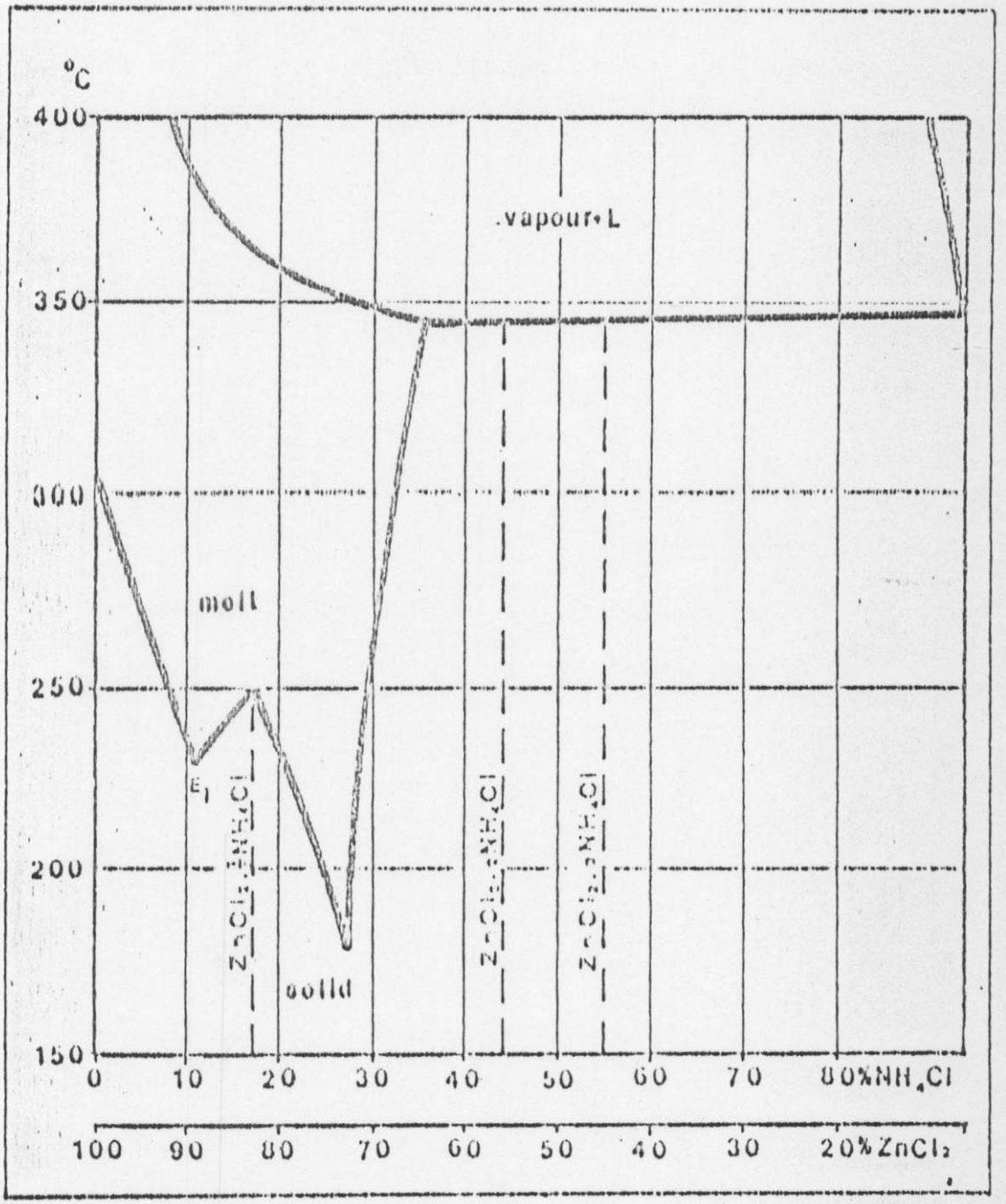

Fig. 7 . The $ZnCl_2$ — NH_4Cl phase diagram.

summarized in the following Tables.

Table 1 : Results of evaluation of NML-Metasave vis-a-vis existing product in Sheets Mill of Tata Steels

Parameters	Existing Inhibitor	Metasave
Acid consumption rate, kg/ton of steel pickled	48.70	29.40
% Metal loss	1.70	1.26
Fume evolution	Moderate	less
Inhibitor consumption rate ml/ton of steel pickled	47.7	92.8

The total annual savings based on installed capacity of 160,000 tons pickling of steels was calculated to be ≃ 1.00 crore. This included total steel and acid savings minus the additional cost of the Metasave in terms of money.

Table 2 : Results of trial of NML-Metasave in pickling line of Tinplate Company of India Ltd. (TCIL)

Parameters	Existing Inhibitor	Metasave
Acid consumption rate, kg/ton of steel pickled	31.99	30.97
% Metal loss	1.40	0.96
% Rejection	3.70	2.90
Fume generation	More	less
Inhibitor consumption lit./ton	0.08	0.05

Based on the above data, it was estimated that the annual saving to the Company was of the order of 19.4 lakhs. The total installed capacity of the plant was 48,000 MT annuam.

Table 3: Results of plant scale evaluations of NML-Metasave vis-a-vis the product then used in the pickling line of Rourkela Steel Plants

Parameters	Existing Inhibitor	Metasave
% Metal loss	1.08	0.717
Quality of pickled product	Good	Good
Fume generation	Perceptible	Negligible
Formation of mono hydrate sulphate	Observed	Nil

Based on the above data, it was evaluated that for a total installed capacity of 172000 tons/year, the expected saving was of the order of 1.03 crores/annum. Details of calculations given in Report No. RDCIS-R&D 23.02.1244.89 Feb. 89.

Table IV:

RESULTS ON IRON ANALYSIS OF PICKELD AND WATER FINSED SPECIMEN EXPOSED TO DIFFERENT SURFACE ACTIVE REAGENTS

SEQUESTERING AGENT	IRON DETACHED (gm/m^2
SA_1	0.48
SA_2	1.70
SA_3	1.12
SA_4	1.30
*RW	6.15

* - RINSED WATER

* SA1 IS MOST EFFECTIVE IN SEQUESTERING OF IRON AND ALSO ACTS AS INHIBITOR.

* SA2 ALTHOUGH ACTS AS A GOOD SA BUT ACCELERATES CORROSION OTHERS HAVE CORROSIVE EFFECT

Table - V

EFFECT OF SURFACE-ACTIVE AGENT ON SEQUESTERING ABILITY OF SA

SEQUESTERING AGENT	IRON CONTENT LEFT ON THE SURFACE (mg/m^2)
SA1	4.8
SA1+ (SURFACTANT)1	0.8
SA1+ (SURF.)2	1.4
SA1+(SURF.)3	3.2

The samples were boiled in distilled water after exposure to SA and solution was analysed for the iron. The table shows that the addition of surfactant is beneficial.

TABLE - VI

Parameters	Galvaflux	Conventional
Dross generation a)g/m^2 galvanized surface b)Kg/mT of galvanized tube	 108 8.60	 128 10.369
Pollution	Negligible	More
Consumption rate a) g/m^2 b) Kg/mT	 17.18 1.37	 34.69 3.46
Corrosivity to steel (mpy)	18	42
Space for storage	one third of conventional	
Packing	One pack	Double Pack
Boiling Temperature	$\approx$ 350°C	Not fixed